Comparative Study of the Storage Stability between a Melamine-Urea-Formaldehyde and a Urea-Formaldehyde Resin

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Abstract

Amino resin wood adhesives used for medium-density fiberboard (MDF), a melamine-urea-formaldehyde (MUF) resin and a urea-formaldehyde (UF) resin, were each synthesized with an overall formaldehyde/urea molar ratio of 1.10. The storage stability of the resins was monitored by their gel times and viscosity changes, as well as by a multiple light scattering method. The storage stability tended to be affected by the temperature at which the resins were stored. MUF resin had a higher storage stability at a storage temperature above room temperature, whereas UF resin exhibited the best storage stability at 10°C with overall good stability at all tested temperatures from 10°C to 40°C.

Melamine-urea-formaldehyde (MUF) resin and urea-formaldehyde (UF) resin are oligomeric condensates of the chemical reaction between formaldehyde and melamine or urea. Owing to their fast curing and good performance, MUF and UF resins have been used for the last few decades as thermosetting wood adhesives in manufacturing interior-use wood-based composite panels, such as medium-density fiberboard (MDF) and particleboard (PB). Their main drawback is low water resistance, leading to formaldehyde emission from wood-based composite panels. Formaldehyde emission from interior-use wood-based composite panels is one of the suspected factors underlying sick house syndrome in newly constructed buildings. Therefore, formaldehyde emission has become one of the most important topics about MUF and UF resins in recent years (Myers and Koutsky 1987, Kim 2001, Park et al. 2009).

Formaldehyde emission from wood-based composite panels has been effectively reduced by lowering the overall molar ratio of formaldehyde to urea (F/U) below 1.10. However, this also lowers the storage stability of amino resins. Melamine-formaldehyde (MF) resin is generally made by reacting melamine with formaldehyde in mildly alkaline pH conditions between 7.5 and 8.5, as in the first reaction stage for the UF resin synthesis. Because polymeric melamine resin is very unstable and easily precipitates out of water, the degree of polymerization of MF resin is controlled to lower than dimer stage. In addition, pure MF resin is expensive; it is generally modified with urea in the form of MUF resins. The reaction process in both MUF resin and UF resin synthesis is similar, but the reaction pH is different. In UF resin manufacture, urea is normally added in two portions, and melamine, if used, is added with the second portion of urea. The cooled MUF resin solution is clear and has low viscosity. In the first step of UF resin synthesis, urea is reacted with formaldehyde, producing a variety of hydroxymethylureas. In the second step, the hydroxymethylureas react with each other to form various oligomers. After cooling to room temperature, the UF resin is a turbid and viscous solution. Turbidity of the UF resin is consistent, and viscosity increases very slowly during storage.

The low degree of condensation and precipitation of monomeric species controls the storage stability of the MF resin. Storage temperature may be adjusted to 50°C for a longer shelf life after resin manufacture (Jahromi 1999, Jahromi et al. 1999). During storage, the aging of UF resins

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involves chemical changes, but MUF resins change less compared with UF resins (Siimer et al. 2005). Although the storage stability of a melamine resin is better at 50°C for an MF resin, the storage stability of MUF and UF resins are unclear because the chemical species of these resins are different. MUF polycondensate chains increase linearly through reactions with unreacted ureas during the storage period, leading to the much longer shelf life of the MUF resin (Zanetti and Pizzi 2003). In general, the lower amount of formaldehyde used in the MUF and UF resins increases the rate of viscosity and leads to higher turbidity due to a decrease in the reactive chemical species. However, the storage stability of these resins at various temperatures has not been explored in detail. Therefore, this study was conducted to investigate storage stability of MUF and UF resins. To gain insight into the physical properties of the resins, we adopted an instrument for characterization of the dispersion state, Turbiscan, which uses a multiple light scattering method to monitor the storage stability of amino resins as a function of turbidity. In addition, viscosity change of resins was measured using Brookfield viscometers at 25°C, and gel time change was measured at regular intervals by using common laboratory methods.

Materials and Methods

MUF [$F/(U + M) = 0.91$] resin with a 1.10 molar ratio of F/U was prepared by adding 465 g (5.73 mol) of a 37 percent solution of formaldehyde in water. The pH was adjusted and kept at 10.8 with a 20 percent NaOH–water solution and heated to 75°C. Then, 20 percent of melamine (195 g, 1.53 mol) based on total amount of synthesized resin, was added, and the temperature was increased to 90°C and maintained for 30 minutes. The first portion of urea (210 g, 3.47 mol) was added and the pH was adjusted to 6.3 with a 20 percent formic acid–water solution. The second portion of urea (106 g, 1.74 mol) was then added when the desired viscosity of the reaction mixture was reached. The reaction mixture was cooled to 25°C and adjusted to pH 8.37 with a 20 percent NaOH–water solution.

UF resin with an overall F/U molar ratio of 1.10 was also synthesized by the following method. The calculated amount of formaldehyde with an initial F/U molar ratio of 2.0 was placed in a four-neck flask and adjusted to pH 7.5 with a 20 percent NaOH–water solution. Once heated to 90°C, the first portion of urea was added. The temperature of the reaction mixture was maintained at 90°C for 30 minutes. Then, the reaction mixture was adjusted to pH 4.8 and reacted at the same temperature until the desired viscosity was reached. The second portion of urea was added before the reaction mixture was cooled to 25°C, and the pH of the solution was adjusted to 8.78 with a 20 percent NaOH–water solution.

Samples of both resins were stored at 10°C, 25°C, and 40°C. Two samples of each resin stored at different temperature conditions were monitored with a Turbiscan EXPERT at 40-μm intervals. Viscosity change of resins stored at 25°C was measured with a Brookfield viscometer DV II+, spindle number 2 at 60 rpm. Gel time change of resins was measured at 100°C by using a Sunshine Gel Timer.

Results and Discussion

Synthesized MUF resin with 60.5 percent nonvolatile solids content, specific gravity of 1.24 g/mL, viscosity of 98.0 mPa, and 75-second gel time, and UF resin with 58.0 percent nonvolatile solids content, specific gravity of 1.19 g/mL, viscosity of 111.3 mPa, and 94-second gel time were used for the storage stability test.

MUF resins stored at different temperatures had different appearances. The resin lost its transparency and became opaque white within 2 hours of storage at 10°C. The opacity lasted for the entire test period without noticeable change. The resin became milky white after storage for 2 days at 25°C and later separated into a clear upper part and an opaque white lower part. Otherwise, the resin stored at 40°C was unchanged and transparency endured for the test period.

With Turbiscan, measurements are expressed as the transmission flux (ΔT) and the backscattering flux (ΔB); ΔT represents the change of turbidity and the ΔB expresses the change of opacity of the resin. As shown in Figures 1 and 2, ΔT of the MUF resin solution was unchanged during storage and ΔB increased slowly at 10°C. MUF resin was a clear solution when the reaction terminated, but it became a turbid viscous gel when stored for 1 day at 10°C, with the change visible by eye. The turbidity of the gelled state lasted for the test period, while the viscosity as well as the opacity of the gel gradually increased. MUF resin contains various types of reactive chemical species, such as hydroxymethylmelamines, hydroxymethylureas, melamine-urea co-con-

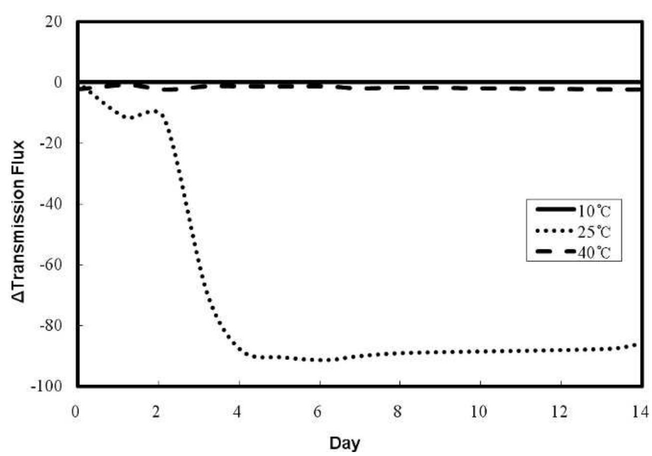

Figure 1.—Transmission scattering depending on storage temperature of melamine-urea-formaldehyde resin.

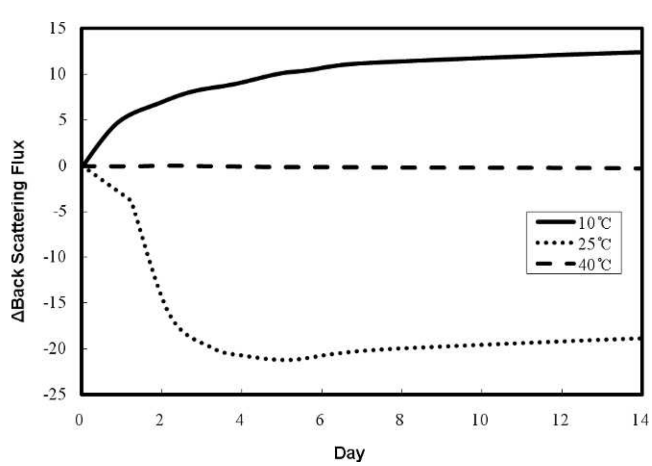

Figure 2.—Backscattering depending on storage temperature of melamine-urea-formaldehyde resin.

densates, unreacted melamines, and unreacted ureas. The transmission of light through the resin solution was not changed because the free movement of those species could be stopped at 10°C. Meanwhile, backscattering of scanned light increased gradually due to whitening of the resin solution caused by increased physical bonds between stopped species. Consequently, the ΔB of the resin increased gradually during the storage period.

Free movement of chemical species in MUF resin is more active at 25°C than at 10°C. Coagulation of reactive species caused by Brownian movement begins, and phase separation of the resin solution slowly occurs by sedimentation of the colloidal particles. Infrared light, which scans the resin solution, may be captured and slowly weaken in the solution. As a result, ΔT and ΔB diminished until the fourth day and afterward showed negative values.

In general, chemical species can be more unstable at high temperatures than at low temperatures because they are more active at high temperatures. However, chemical species in the MUF resin stored at 40°C were very stable. The chemical species in the resin were maintained at a good chemical balance and no other secondary reactions occurred. For that reason, the ΔT and the ΔB values of the MUF resin stored at 40°C were unchanged until the 14th day. Thus, we concluded that the optimal storage temperature of the MUF resin is at 40°C. The storage stability of MUF resin can be influenced by other factors, such as degree of condensation or pH of resin solution, but these other factors were not considered during this study.

Unlike MUF resin, the storage stability of UF resin was mostly unaffected by storage temperature, although it had slightly better stability at 10°C than at 25°C and 40°C. As shown in Figures 3 and 4, the ΔT and the ΔB of the UF resin changed most significantly between the second and fourth days of the storage period due to the rapid turbidity increment. Afterward, the ΔT decreased and the ΔB increased slowly at every storage temperature. The UF resin stored at 10°C showed the least change in the ΔT and ΔB values due to the most stable balance of various chemical species in the resin.

Figure 5 shows the viscosity changes of the MUF and UF resins stored at 25°C based on storage times. The viscosity of the MUF resin increased in an approximately linear fashion due to physical interactions of various species in the resin from the 2nd to the 14th day of storage. In contrast, the UF resin exhibited little change in viscosity, showing only a slight increase during the whole storage period. These results imply that the storage stability of MUF resin decreased as time elapsed.

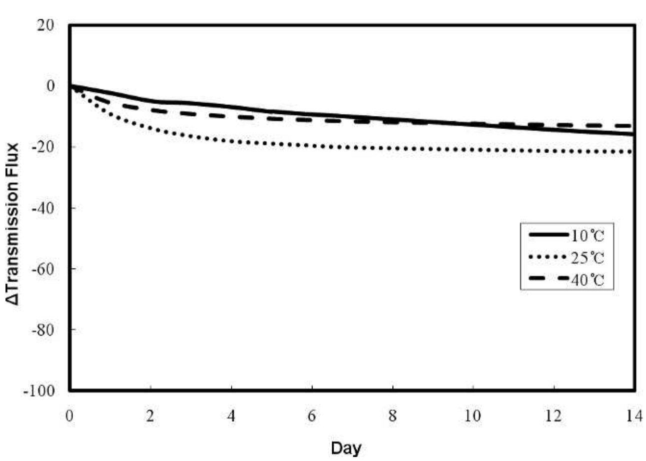

Figure 3.—Transmission scattering depending on storage temperature of urea-formaldehyde resin.

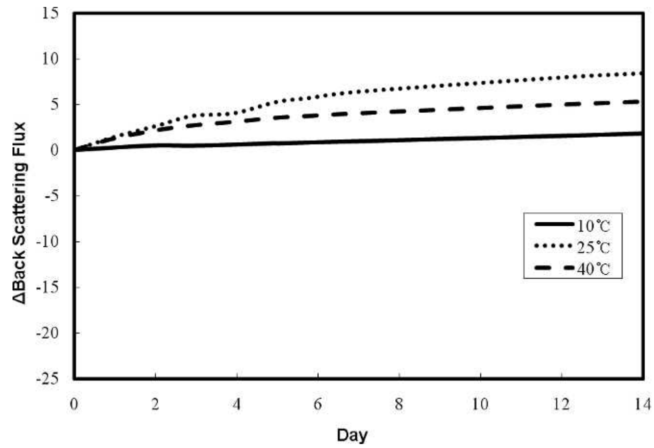

Figure 4.—Backscattering depending on storage temperature of urea-formaldehyde resin.

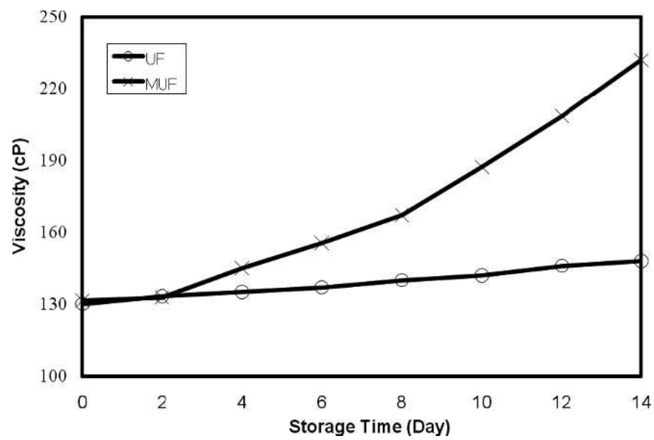

Figure 5.—Viscosities of melamine-urea-formaldehyde (MUF) and urea-formaldehyde (UF) resins depending on storage time.

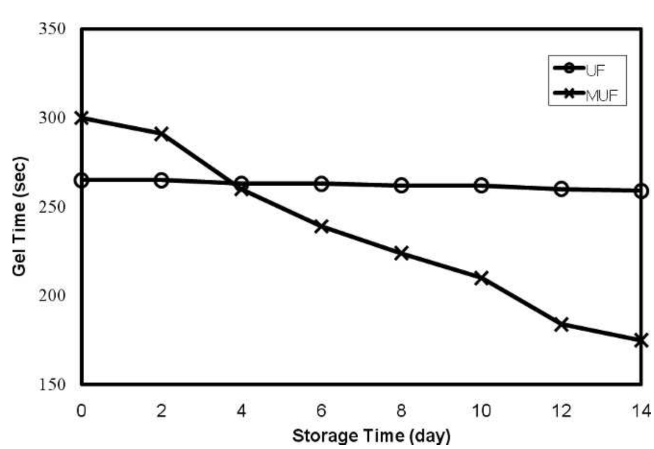

Figure 6.—Gel times of melamine-urea-formaldehyde (MUF) and urea-formaldehyde (UF) resins depending on storage time.

Gel times of the MUF resin based on the storage time are presented in Figure 6. There is an obvious contrast between the MUF resin and the UF resin gel times. The gel time of the MUF resin decreased as time elapsed and it was prominent only for the MUF resin. The gel time of the UF resin barely changed.

Our results for viscosity and gel time may be attributed to the chemical structure of melamine. Because melamine molecules have three reactive amino groups, each amino group can react with up to 2 mol of formaldehyde to form various hydroxymethylolated melamines. As a result, the MUF resin solution may have a more branched structure in the resin solution. For that reason, the physical interactions, such as hydrogen bonding and pi-stacking interaction among the hydroxymethylated melamines, are greater than those of the hydroxymethylated ureas. Therefore, the movement of each hydroxymethylated melamine in the MUF resin might be restricted in comparison with hydroxymethylated ureas in the UF resin. Consequently, the viscosity for the MUF resin would increase and the gel time decrease, but the viscosity and the gel time of UF resin would remain stable.

Conclusions

The storage stability of an MUF resin and a UF resin was monitored, and it was found to be affected by storage temperature. MUF resin was more stable at the higher temperatures than UF resin; however, UF resin was stable at all tested temperature ranges compared with MUF resin. Therefore, we conclude that the storage temperature of MUF resin must be controlled more accurately to ensure long lifetime.

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